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Abstract

A detailed chemical kinetic reaction mechanism has been developed for a group of four small alkyl ester fuels, consisting of methyl formate, methyl acetate, ethyl formate and ethyl acetate. This mechanism is validated by comparisons between computed results and recently measured intermediate species mole fractions in fuel-rich, low pressure, premixed laminar flames. The model development employs a principle of similarity of functional groups in constraining the H atom abstraction and unimolecular decomposition reactions for each of these fuels. As a result, the reaction mechanism and formalism for mechanism development are suitable for extension to larger oxygenated hydrocarbon fuels, together with an improved kinetic understanding of the structure and chemical kinetics of alkyl ester fuels that can be extended to biodiesel fuels. Variations in concentrations of intermediate species levels in these flames are traced to differences in the molecular structure of the fuel molecules.

Keywords: Reaction mechanisms, laminar flames, oxygenates, kinetic modeling

1. INTRODUCTION

Concerns about long-term availability of conventional petroleum-based fuels, the continuing need to reduce harmful emissions of atmospheric pollutants, and the urgency of reducing emissions of greenhouse gases are all creating interest in various types of renewable biofuels. One important class of biofuels consists of large methyl and ethyl esters derived from vegetable and other oils [1]. These biofuels operate well in diesel and HCCI engines, with another attractive feature that the oxygen atoms imbedded within the biodiesel fuel molecule help reduce soot production from diesel engines [2,3].

While an enormous number of kinetic studies have been published on the subject of hydrocarbon kinetics, few experimental or kinetic modeling studies have been carried out for alkyl ester molecules, which severely limits our ability to predict their combustion properties, such as heat release rates, amounts of pollutant emissions, types and levels of intermediate species, and ignition properties. Most practical biodiesel fuel molecules, including soy and rapeseed biodiesel fuel, are methyl esters with as many as 16 - 18 carbon atoms in the form of a long, straight chain, either saturated or with 1 - 3 double bonds in the long chain. The large size of such molecules has been an impediment to the development of detailed kinetic models for them. A recent study describes a detailed kinetic model for methyl decanoate [4], a large methyl ester with a carbon chain containing ten C atoms, and several other recent kinetic modeling studies [5-9] have examined the kinetics of small methyl and ethyl esters with chains of 2 to 4 carbon atoms. The present work is part of a systematic approach towards a better kinetic understanding of alkyl ester fuels, focusing attention on the kinetic description of the essential ester portion of such fuel molecules and showing how that ester moiety influences the

combustion characteristics of the hydrocarbon portions of those fuels. Our intent is to reduce the complexity associated with large biodiesel fuels by combining detailed experimental and kinetic modeling studies of low pressure, fuel-rich, laminar, premixed flames with four different small alkyl ester fuels. Models for combustion chemistry of small molecule analogs for larger biodiesel molecules will then be valuable in developing models for larger, full-size biodiesel molecules.

Historically, validations of detailed kinetic models have emphasized simulations of homogeneous environments such as shock tubes or rapid compression machines, but simulations of laminar flame structure have not been very useful as validation tests. However, current experiments are now able to quantify spatial variations in mole fractions of many reactant, product and intermediate species, including some important radicals, within low pressure flames, all of which are much more demanding tests of kinetic models than are laminar burning velocities, representing an important advance in the type of experimental tools available for kinetic research.

2. FUELS STUDIED AND KINETIC REACTION MECHANISMS

Four very similar small methyl and ethyl ester fuels were used in the present study, consisting of methyl formate ($\text{C}_2\text{H}_4\text{O}_2$, $m/z = 60$), methyl acetate ($\text{C}_3\text{H}_6\text{O}_2$, $m/z = 74$), ethyl formate ($\text{C}_3\text{H}_6\text{O}_2$, $m/z = 74$) and ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$, $m/z = 88$). Spatial variations in mole fractions of 28 different stable and radical species for the $m/z = 74$ structural isomers methyl acetate and ethyl formate were reported in an experimental study by Osswald et al. [10], and spatial profiles for the other two fuels have been measured by the same experimental group [11]. Both studies discussed possible reaction pathways and their relationships with structures for methyl acetate and ethyl formate, although no kinetic modeling was carried out.

Few detailed kinetic mechanisms have been reported for any of these fuels. Kinetic mechanisms for a larger methyl ester, methyl butanoate ($\text{C}_5\text{H}_{10}\text{O}_2$, $m/z = 102$) have been developed [5-7,12,13], in part to see if methyl butanoate could be useful as a surrogate for modeling biodiesel combustion. In addition, Metcalfe et al. [7] developed a detailed kinetic mechanism for high temperature oxidation of ethyl propanoate ($\text{C}_5\text{H}_{10}\text{O}_2$, $m/z = 102$), a structural isomer of methyl butanoate, and Walton et al. [13] have very recently reported experimental rapid compression machine (RCM) studies of both methyl butanoate and ethyl propanoate with kinetic mechanisms that describe oxidation in RCM and shock tube conditions [7] over a temperature range from 930 - 1670K.

Dagaut et al. [9] studied methyl acetate oxidation in a jet-stirred reactor and developed a kinetic mechanism, largely based on structural similarities between methyl acetate and related species including methanol, dimethyl ether, and ethane. Gasnot et al. [8] developed a detailed kinetic oxidation mechanism for ethyl acetate, with

submechanisms for vinyl acetate and acetic acid, to study stoichiometric methane/air flames with additions of 1, 2 and 3% ethyl acetate. They also employed similarities between ethyl acetate and other species to build their detailed kinetic mechanism. Good and Francisco [14] carried out an extensive analysis of methyl formate and dimethyl ether oxidation, using ab initio techniques, to provide kinetic insights into important reaction pathways for methyl formate oxidation.

The present kinetic modeling study uses a similar approach to develop detailed mechanisms for four small ester species, and the goal is to produce a single, internally self-consistent mechanism for all of these alkyl ester fuels that emphasizes their structural similarities. In addition to the present four flames, this mechanism then provides a base and set of kinetic rules on which to build mechanisms for larger esters in future studies.

The four ester fuels of this study are shown schematically in Figure 1, illustrating their strong structural similarities. All have the central -O(C=O)- group, and each has either a methyl or ethyl group attached to the O atom and either an H atom (in the formates) or methyl radical (in the acetates) bonded to the C=O structure; these structural similarities have been exploited in the construction of the present mechanism.

Consumption of these ester fuels is accomplished either via unimolecular decomposition or by abstraction of individual H atoms by radical species. Rates of both fuel consumption pathways depend in predictable ways on the structure of the fuel molecule, and especially on the strength of the bond being broken. Bond strengths depend on electronic structure in the vicinity of that bond, so in practical terms, they depend on the identities of the neighboring atoms close to the bond being broken.

Figure 1 shows that the ethyl groups in ethyl formate and ethyl acetate have C-H bond strengths that must be close to identical, since both have CH₂ groups bonded to methyl and -O(C=O)- groups, and their CH₃ groups are bonded to -CH₂O(C=O)- groups. Therefore, we have assumed that H atom abstraction reactions from these ethyl groups have identical rates with each radical reactant. The same logic applies to H atom abstraction reactions from the methyl groups in methyl acetate and methyl formate, to H atom abstraction reactions from the formate group H atom in methyl formate and ethyl formate, and to H atom abstraction reactions from the acetate groups in methyl acetate and ethyl acetate. Preliminary H atom abstraction rates were estimated based on reactions in molecules with similar molecular structures, and then revised by comparisons with experimental results as described below.

For methyl acetate and methyl formate, unimolecular decomposition initiation reactions involve breaking a C-O bond to produce methyl or methoxy radicals. However, for ethyl esters, another unimolecular elimination reaction producing ethene is also observed as shown in Figure 2, via a six-membered transition state ring, with a rate rapid enough to contribute significantly to fuel consumption. Consistent with this analysis, Metcalfe et al. [7] observed that ethyl propanoate ignited much more rapidly in shock tube experiments than its structural isomer, methyl butanoate, because ethyl propanoate was consumed by a rapid ethene molecular elimination reaction like those in Fig. 2, while methyl butanoate, like methyl acetate and methyl formate in the present study, did not have such a rapid molecular elimination reaction. Since the transition states for both ethene elimination reactions are the same in the ethyl esters, the rates of both initiation reactions are assumed to be equal, with an activation energy of 50 kcal/mol equal to that

for ethyl propanoate [15], and an A-factor of 1.0×10^{13} close to the value of 4.0×10^{12} estimated by O'Neal and Benson [16].

3. EXPERIMENTS

The experiments with these four small alkyl ester fuels have been discussed in considerable detail in recent papers [10,11], so they will be summarized briefly here. A flame-sampling molecular-beam mass spectrometer, employing tunable vacuum-ultraviolet synchrotron radiation for photoionization was used to study these premixed, low-pressure (30 Torr) flat flames [10]. The essential features include a low-pressure flame chamber, a differentially pumped molecular-beam flame-sampling system, and a linear time-of-flight mass spectrometer (TOFMS), coupled to a 3-m monochromator used to disperse synchrotron radiation at the Advanced Light Source of the Lawrence Berkeley National Laboratory. Flame gases are sampled by a quartz cone along the axis of the flat flame burner, and the burner can be moved toward or away from the sampling cone to make measurements at different distances within the flame.

A molecular beam from the sampling system is then crossed by the dispersed VUV light from the monochromator, and photoions are collected and mass-analyzed with a TOFMS with a mass resolution of $m/\Delta m = 400$ and finally converted into spatial profiles of specific chemical species. The experiments can discriminate between isomers at many mass numbers, based on differences in ionization energies, although some combinations of signals are very difficult to separate when their ionization energies are very similar. Osswald et al. [10] estimated the experimental uncertainties in major

species as ± 15 -20%, most intermediate species as ± 30 -40% and radical species as uncertain by factors of 2-4.

Flame temperatures for the methyl formate and ethyl acetate flames were measured using laser-induced fluorescence (LIF) from OH, while temperatures for the methyl acetate and ethyl formate flames were measured in separate experiments at Bielefeld University using laser-induced fluorescence of seeded NO (0.5%). The fluorescence measurements were carried out under flame conditions unperturbed by the sampling cone, and the “distance from the burner” used by Osswald et al. [10] and in this study is taken to be 0.9 mm (4.5 sampling orifice diameters) less than the actual separation between the burner and the tip of the sampling cone. The shift was introduced to match the mole fraction profiles of the measured data with the model and is well within the expected limits for uncertainty in the measured burner-to-cone separation and uncertainty in the shift needed to account approximately for the fact that the probe samples gases slightly upstream of the sampling cone orifice [10]. The four temperature profiles from these studies are shown in Figure 3 and are also available in digital format as supplementary material in Table S1.

4. COMPUTED RESULTS

Flame models were computed for the four ester flames, using the Chemkin 4.0 software [17]. These problems used the burner-stabilize flame option in which the experimentally measured temperatures are specified and the energy equation is not solved. The inlet boundary condition specifies the mass fluxes of each species and the exit boundary assumes a zero gradient in the mass fractions. Transport parameters for ester fuels and their intermediate species were estimated from species of similar size and structure for which parameters were available. A mixture averaged transport model was used in the flame calculations. A minimum of 200 computational zones were used to ensure sufficient resolution of each flame. Inlet flow conditions for each flame are summarized in Table 1. All four flames are fuel-rich and diluted by argon, and in each model calculation, the spatial temperature was specified, so the energy equation was not solved in the Chemkin simulation.

An initial reaction mechanism was prepared for each of these fuels, built on a recent C₁-C₄ mechanism from Curran et al. [18]. A kinetic submechanism for acetic acid, a major product of ethyl acetate consumption, was taken from Gasnot et al. [8] and included here. Computed species profiles were then compared with experimental values, with mixed initial results. Sensitivity analysis and reaction path analysis were used to modify the reaction rate parameters to arrive at an optimized set of rate parameters. The only reaction rate parameters directly involving the ester fuel molecules that showed significant sensitivities were H atom abstraction reactions with H, OH and HO₂ and the unimolecular decompositions. However, the most significant sensitivities in the four flame calculations involved the different reaction flux pathways available for each fuel,

following H atom abstractions at different sites in the fuel molecule, as discussed below. For each flame, the major species CO, CO₂, H₂, H₂O, O₂ and fuel were reproduced very well, as illustrated for the methyl formate flame in Figure 4.

4.1 Methyl acetate

Methyl acetate (MA) contains two different methyl radicals, each with somewhat different C-H bond strengths, and different model compounds were used to estimate H atom abstraction rates. Rates of H atom abstractions from the methyl radical bound to the O atom in the ester group were taken from the structurally similar methyl radical in methyl butanoate [5,6]. The other methyl in methyl acetate is influenced by the adjacent C=O group and has a C-H bond energy (97.7 kcal/mol [15]) similar to that for the tertiary C-H bond in methyl cyclohexane (96.5 kcal/mol) [19], which was used as the initial model compound. Abstractions from the two methyl groups lead to different intermediate species. The $\bullet\text{CH}_2\text{O}(\text{CO})\text{CH}_3$ (Path 1) radical decomposes via β -scission to produce formaldehyde and acetyl, and the acetyl rapidly decomposes to produce methyl and CO, although a small percentage of the acetyl radicals recombine with methyl radicals to produce acetone. In contrast, the $\text{CH}_3\text{O}(\text{CO})\text{H}_2\text{C}\bullet$ (Path 2) radical decomposes to produce ketene and the methoxy radical. The methoxy radical can produce methanol by abstracting another H atom from the fuel, recombine with methyl to produce dimethyl ether, or decompose to produce formaldehyde and H atoms. Ethene is produced only via methyl/methyl recombination followed by ethane dehydrogenation. Thus Path 1 produces all of the acetone and most of the formaldehyde in this flame, while Path 2 produces all of the ketene and dimethyl ether, and both paths lead to relatively small levels of ethene.

The initial reaction rates were found to produce excessively high levels of ketene and dimethyl ether, but reasonably accurate levels of most of the other intermediate species. The H atom abstraction rates for Path 2 were all therefore reduced, simply by

reducing the A factors by a factor of almost 10 in each rate expression, leading to the computed results shown in Figure 5 for the MA flame. The Path 1 H abstraction reaction rates produced excellent agreement for intermediate species predictions without further modification, confirming that the use of rates from the same structural group in methyl butanoate can be transferred intact to methyl acetate with very good accuracy. Use of Path 2 reaction rates from a methyl radical in a differently structured molecule introduced rate expressions that required corrections based on comparisons with experimental results.

4.2 Ethyl formate

The same approach was used for initial H atom abstraction rates in ethyl formate (EF). Rate expressions for H atom abstraction producing n-propyl and iso-propyl radicals from propane [18] were used as the initial estimates of analogous reaction rates of the ethyl radical in EF. Similarly, H atom abstraction rates in the weak C-H bond in the formate part of EF were estimated based on secondary H atom abstractions in methyl cyclohexane [19].

As with MA, different H atom abstraction paths in EF produce different intermediate species. The primary H atom abstraction Path 3 produces ethene and CO₂, the secondary H atom abstraction Path 4 produces acetaldehyde and CO, and the formate H abstraction Path 5 produces CO₂ and ethyl, which rapidly produces ethene. Computed results with the initial EF submechanism predicted levels of methane, acetaldehyde and formaldehyde too high by factors of 2-4, while predictions of ethene, ketene, and acetylene were too low by similar factors. Best overall agreement between the computed and experimental mole fraction profiles was found when rates for H abstractions via Path

3 were increased by a factor of 2, those for Path 4 were decreased by a factor of 4, and those for Path 5 decreased by a factor of 2, with those results shown for selected species in Figure 5. The need for these rate adjustments reflects the fact that the C-H bonds in the different model compounds are different from those in ethyl formate.

4.3 *Ethyl acetate and methyl formate*

Ethyl acetate and methyl formate contain the same functional groups as ethyl formate and methyl acetate, all based on a central -O(C=O)- group, but with the ethyl and methyl groups interchanged. Therefore, the initial submechanisms for ethyl acetate and methyl formate assumed that the H atom abstraction rates in each of the functional groups are exactly the same as those in the first pair of fuels. The subsequent decomposition products of each radical in ethyl acetate and methyl formate are different from the analogous radicals in ethyl formate and methyl acetate, and comparisons between computed and experimental species profiles must show whether or not the similarities in H abstraction rates can be translated into accurate predictions of intermediate species.

There are three H atom abstraction pathways in ethyl acetate, originating with abstraction of the primary H atom (Path 6) and the secondary H atom (Path 7) in the ethyl group and the acetyl H atom (Path 8) from the acetyl group. Path 6 produces ethene as its most important signature, Path 7 produces acetyl radicals and stable acetaldehyde, and Path 8 produces ketene and the ethoxy radical.

Similarly, there are two H atom abstraction pathways in methyl formate, the first being the methyl group and the second consisting of the formate H atom bonded to the

C=O group. Abstraction of an H atom from the methyl group (Path 9) leads to formaldehyde and a formyl radical, while abstraction of the formate H atom (Path 10) produces methyl and CO₂.

Comparisons between computed and experimentally measured intermediate species concentrations are shown for selected species in Figure 5 for the initial families of H atom abstraction rates, with overall excellent agreement. Subsequent optimizations produced very minor changes in the overall agreement between the computed and experimental results. The final rate expressions for all four ester fuels are provided as supplementary material in Table S2, and the entire mechanism, thermochemical data, and transport data are available on the LLNL webpage [20].

These results for H atom abstraction rates should not be surprising. The electronic structure and C-H bond strengths in the CH₃CH₂O(C=O)- group are not very different when the final group is an H atom or a methyl radical, so the abstraction rates in the similar groups should be nearly equal. Confirmation is provided by a recent theoretical study by Sumathi and Green [21] who found that secondary C-H bond strengths in the ethyl radical part of ethyl formate and ethyl acetate differ by only 0.3 kcal/mol. The same similarities exist for the C-H bond strengths in the CH₃O(C=O)- group and for the -O(C=O)H and -O(C=O)CH₃ groups, again in good agreement with theoretical results of Sumathi and Green, and the excellent overall agreement in the present results confirms this view.

5 DISCUSSION

Figure 5, column a, shows the mole fractions of the C_2 species, ethene and acetylene, in the four flames. The EA and EF flames produce much higher levels of these species, since ethene is produced directly from the ethyl groups, while the MA and MF fuels must produce C_2 species by methyl recombination followed by dehydrogenation. Acetylene peaks farther from the burner than ethene in both experiments and model calculations, consistent with the fact that acetylene is produced from ethene, and the peak values of acetylene are lower than peak ethene levels except in the experimental MA flame results.

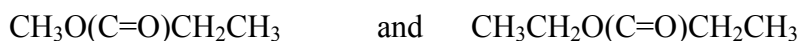
Figure 5, column b, shows the same type of relationship between formaldehyde and formyl radical in all four flames, with peak formyl values following those of its parent formaldehyde. Absolute levels of both species are in excellent agreement between experimental and computed values. In contrast with the C_2 species, the MA and MF flames produce much higher levels of formaldehyde than the ethyl esters, since formaldehyde is an immediate β -scission product from H atom abstraction from the methyl group.

The products of H atom abstraction from the acetate group, followed by β -scission, can be seen from Figure 5, column c, showing much higher ketene levels from EA and MA than from the formates. The acceptable agreement between computed and measured levels of propyne suggest that the reaction mechanisms can be extended to future studies of soot formation from ester fuels, and the relative amounts of propyne production reflect the importance of C_2 species in propyne formation and soot production.

Methane is produced as a major intermediate in all four flames from methyl radicals that abstract H atoms from the fuel, and the excellent agreement between computed and measured levels of methane in Figure 5, column d, indicates that the methyl radical values are being predicted accurately. Acetaldehyde production follows a variety of rather complicated pathways in these flames, directly in the EA flame and by H atom abstraction by acetyl radicals in the EA and MA flames. Agreement between computed and experimental values is very good and provides additional validation of the kinetic mechanisms.

Finally, experimental results for a considerable number of species for all four flames in Fig. 5 show high values at locations near the burner that cannot be reproduced by the kinetic models. These differences suggest possible kinetic effects in or on the surface of the burner, or difficulties of making species measurements very close to the burner where the sampling cone may disturb the flows.

One goal of the present work is to establish a core kinetic reaction mechanism for methyl and ethyl esters of increasing complexity. We have noted above that the methyl group H atom abstraction reaction rates in methyl butanoate [5-7] were used without change in the present methyl formate and methyl acetate submechanisms. As another example, reaction mechanisms for methyl and ethyl propanoate



should have the same H atom abstraction rates for the $\text{CH}_3\text{O}-$ and $\text{CH}_3\text{CH}_2\text{O}-$ portions of those molecules as those developed above. Only the H atom abstraction rates from the propanoate $-\text{O}(\text{C}=\text{O})\text{CH}_2\text{CH}_3$ group would be needed as new information, and those rates should be expected to be the same in both methyl and ethyl propanoate. The present

approach can also make mechanism development simpler in cases where the hydrocarbon segment is unsaturated, such as methyl crotonate [22] or methyl and ethyl propenoate.

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REFERENCES

1. M. S. Graboski and R. L. McCormick., Prog. Ener. Combust. Sci. 24 (1998) 125-164.
2. N. Miyamoto, H. Ogawa, N. M. Nurun, K. Obata, and T. Arima, Society of Automotive Engineers paper SAE-980506 (1998).
3. C. K. Westbrook, W. J. Pitz, and H. J. Curran, J. Phys. Chem. A 110 (2006) 6912-6922.
4. O. Herbinet, W. J. Pitz and C. K. Westbrook, Combust. Flame, submitted (2007).
5. E. M. Fisher, W. J. Pitz, H. J. Curran, and C. K. Westbrook, Proc. Combust. Inst. 28 (2000) 1579-1586.
6. S. Gaïl, M. J. Thomson, S. M. Sarathy, S.A. Syed, P. Dagaut, P. Dievart, A. J. Marchese and F. L. Dryer, Proc. Combust. Inst. 31 (2007) 305-311.
7. W. K. Metcalfe, S. Dooley, H. J. Curran, J. M. Simmie, A. M. El-Nahas and M. V. Navarro, J. Phys. Chem. A 111(19) (2007) 4001-4014.
8. L. Gasnot, V. Decottignies, and J. F. Pauwels, Fuel 84 (2005) 505-518.
9. P. Dagaut, N. Smoucovit and M. Cathonnet, Combust. Sci. Technol. 127 (1997) 275-291.
10. P. Osswald, U. Struckmeier, T. Kasper, K. Kohse-Höinghaus, J. Wang, T. A. Cool, N. Hansen, and P. R. Westmoreland, J. Phys. Chem. A 111 (19) (2007) 4093-4101.
11. B. Yang, J. Wang, T. A. Cool, A. Lucassen, P. Osswald, U. Struckmeier, K. Kohse-Höinghaus, T. Kasper, N. Hansen, and P. R. Westmoreland, in preparation (2007).
12. D. Archambault and F. Billaud, J. Chim. Phys. 96 (1999) 778-796.
13. S.M. Walton, M.S. Wooldridge and C.K. Westbrook, Proc. Combust. Inst. 32 (2009) in press.
14. D. A. Good and J. S. Francisco, J. Phys. Chem. A 104 (2000) 1171-1185.
15. A. M. El-Nahas, M. V. Navarro, J. M. Simmie, J. W. Bozzelli, H. J. Curran, S. Dooley, and W. Metcalfe, J. Phys. Chem. A 111 (19) (2007) 3727-3739.
16. H. E. O'Neal and S. W. Benson, J. Phys. Chem. 71 (9) (1967) 2903-2921.
17. R. J. Kee, F. Rupley, J. A. Miller, et al., Chemkin Collection, Release 4.0, Reaction Design, Inc., 2007.

18. E. L. Petersen, D. M. Kalitan, S. Simmons, G. Bourque, H. J. Curran, and J. M. Simmie, *Proc. Combust. Inst.* 31 (2007) 447-454.
19. W. J. Pitz, C. V. Naik, T. N. Mhaolduin, C. K. Westbrook, H. J. Curran, J. P. Orme, and J. M. Simmie, *Proc. Combust. Inst.* 31 (2007) 267-275.
20. http://www-cmls.llnl.gov/?url=science_and_technology-chemistry-combustion
21. R. Sumathi and W. H. Green, *Phys. Chem. Chem. Phys.* 5 (16) (2003) 3402-3417.
22. S. M. Sarathy, S. Gail, S. A. Syed, M. J. Thomson, and P. Dagaut, *Proc. Combust. Inst.* 31 (1) (2007) 1015-1022.

Table 1
Flow conditions for ester flames in this study

Fuel	MA	EA	MF	EF
Pressure (torr)	30	30	30	30
Equiv. ratio	1.82	1.56	1.83	1.83
C/O	0.514	0.475	0.477	0.514
Inlet vel (cm/s)	64.0	65.7	66.6	64.0
Fuel slm	0.994	0.686	1.462	0.998
O ₂ slm	1.909	2.200	1.600	1.909
Ar slm	1.000	1.120	1.000	1.000

FIGURE CAPTIONS

1. Methyl and ethyl esters included in this study
2. Schematic of molecular elimination reaction pathways for ethyl formate and ethyl acetate
3. Experimentally measured temperatures for the alkyl esters in this study
4. Measured (symbols) and computed (lines) major species profiles for the methyl formate flame; dashed lines correspond to open symbols.
5. Experimental values (symbols) compared with computed results (lines); dashed lines correspond to open symbols; a) ethene (circles) and acetylene (squares); b) Formaldehyde (circles) and formyl (squares), formyl values have been increased by a factor of 10 for comparison; c) ketene (circles) and propyne (squares), propyne values have been increased by a factor of 10 for comparison; d) methane (circles) and acetaldehyde (squares).

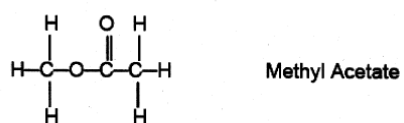
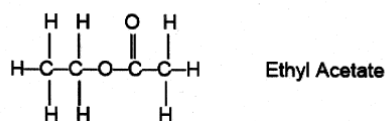
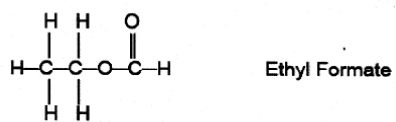


Figure 1 Methyl and ethyl esters included in this study

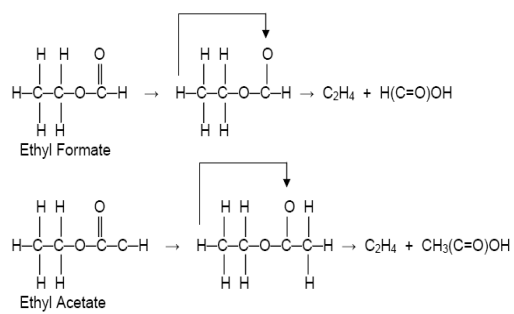


Figure 2 Schematic of molecular elimination reaction pathways for ethyl formate and ethyl acetate

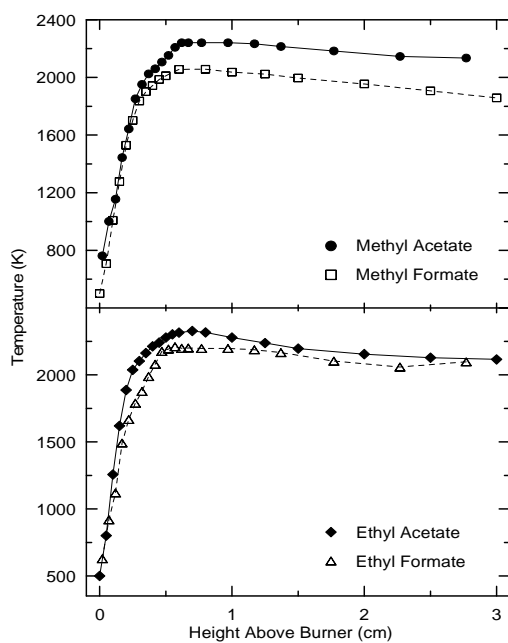


Fig. 3 Experimentally measured temperatures for the alkyl esters in this study

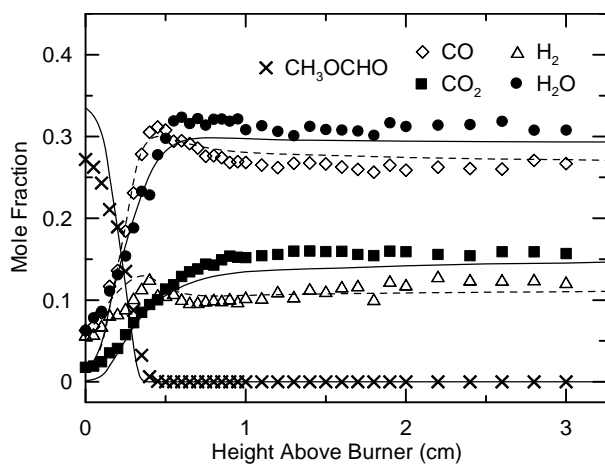


Fig. 4 Measured (symbols) and computed (lines) major species profiles for the methyl formate flame; dashed lines correspond to open symbols.

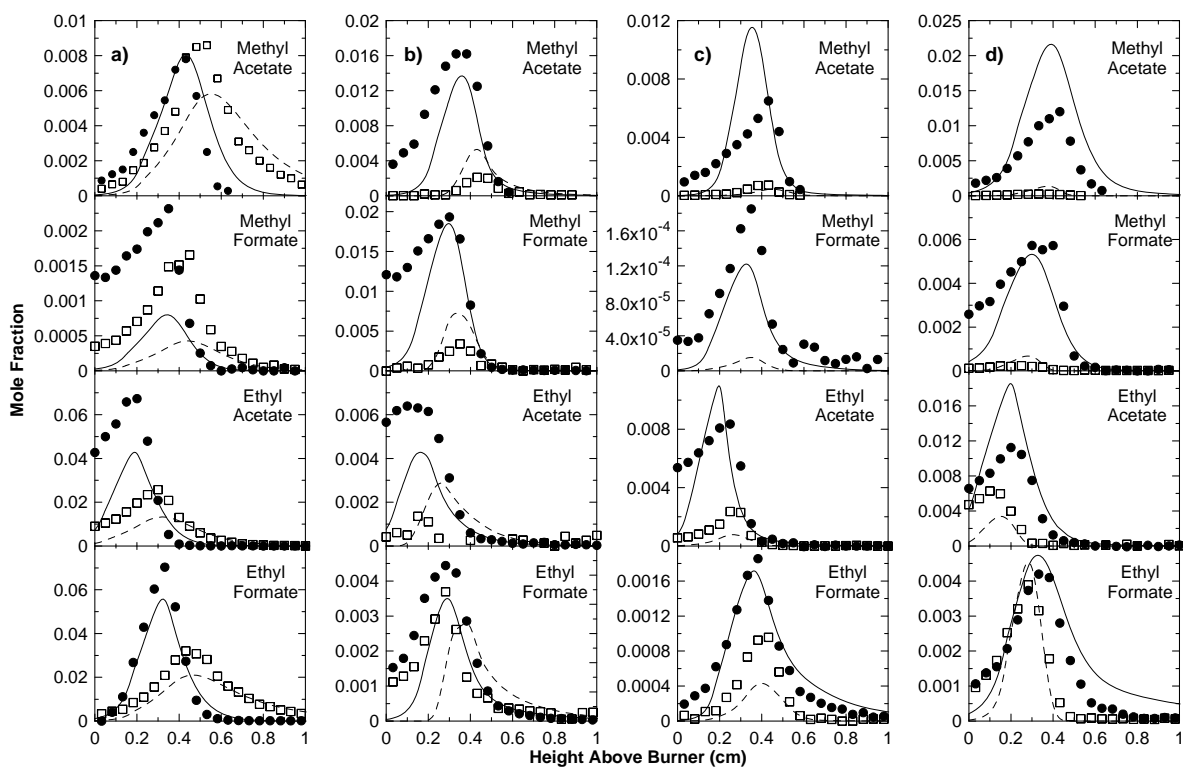


Fig. 5 Experimental values (symbols) compared with computed results (lines); dashed lines correspond to open symbols; a) ethene (circles) and acetylene (squares); b) Formaldehyde (circles) and formyl (squares), formyl values have been increased by a factor of 10 for comparison; c) ketene (circles) and propyne (squares), propyne values have been increased by a factor of 10 for comparison; d) methane (circles) and acetaldehyde (squares).

Supplemental material for (Westbrook et al., A Detailed Chemical Kinetic Reaction Mechanism for Oxidation of Four Small Alkyl Esters in Laminar Premixed Flames, Proc. Combust. Inst. 32, 2009)

Table S1 Temperature profiles for flame modeling

Table S2 Arrhenius parameters for oxidation of Ethyl Formate (EF), Methyl Acetate (MA), Ethyl Acetate (EA) and Methyl Formate (MF). Units are mole, cm, sec, Kelvin, calories.

Table S1 Temperature profiles for flame modeling

Ethyl formate	x - mm	T	Methyl formate	x - mm	T
	0.2	762		0	500
	0.7	1001		0.5	707
	1.2	1155		1	1008
	1.7	1444		1.5	1277
	2.2	1643		2	1529
	2.7	1852		2.5	1702
	3.2	1952		3	1836
	3.7	2025		3.5	1902
	4.2	2060		4	1943
	4.7	2107		4.5	1986
	5.2	2153		5	2012
	5.7	2209		6	2056
	6.2	2241		8	2057
	6.7	2241		10	2037
	7.7	2241		12.5	2023
	9.7	2241		15	1996
	11.7	2234		20	1955
	13.7	2215		25	1907
	17.7	2184		30	1858
	22.7	2146			
	27.7	2135			

Ethyl acetate	x - mm	T	Methyl acetate	x - mm	T
	0	500		0.2	629
	0.5	800		0.7	919
	1	1257		1.2	1120
	1.5	1619		1.7	1492
	2	1887		2.2	1668
	2.5	2038		2.7	1789
	3	2104		3.2	1877
	3.5	2163		3.7	1989
	4	2213		4.2	2080
	4.5	2241		4.7	2176
	5	2279		5.2	2193
	5.5	2303		5.7	2211
	6	2316		6.2	2199
	7	2328		6.7	2201
	8	2317		7.7	2198
	10	2279		9.7	2198
	12.5	2238		11.7	2188
	15	2196		13.7	2167
	20	2155		17.7	2103
	25	2128		22.7	2059
	30	2116		27.7	2098

Table S2

Arrhenius parameters for oxidation of Ethyl Formate (EF), Methyl Acetate (MA), Ethyl Acetate (EA) and Methyl Formate (MF). Units are mole, cm, sec, Kelvin, calories.

Reaction	A	n	Ea
EF+h=EFp+h2	1.88E+05	2.8	6280.0
EF+o2=EFp+ho2	2.00E+13	0.0	47500.0
EF+o=EFp+oh	1.03E+14	0.0	7850.0
EF+oh=EFp+h2o	1.05E+10	1.0	1586.0
EF+ho2=EPp+h2o2	1.68E+13	0.0	20430.0
EF+ch3=EFp+ch4	1.29E+12	0.0	11600.0
EF+c2h3=EFp+c2h4	1.00E+11	0.0	10400.0
EF+c2h5=EFp+c2h6	1.00E+11	0.0	10400.0
EF+ch3o=EFp+ch3oh	3.00E+11	0.0	7000.0
EF+ch3o2=EFp+ch3o2h	1.70E+13	0.0	20460.0
EFp=c2h4+ocho	1.34E+13	-0.4	24610.0
EF+o2=EFs+ho2	4.00E+13	0.0	47500.0
EF+h=EFs+h2	3.25E+05	2.4	4471.0
EF+o=EFs+oh	2.81E+13	0.0	5200.0
EF+oh=EFs+h2o	1.16E+07	1.6	-35.0
EF+ho2=EFs+h2o2	5.60E+12	0.0	17700.0
EF+ch3=EFs+ch4	3.98E+11	0.0	9500.0
EF+c2h3=EFs+c2h4	1.00E+11	0.0	10400.0
EF+c2h5=EFs+c2h6	1.00E+11	0.0	10400.0
EF+ch3o=EFs+ch3oh	3.00E+11	0.0	7000.0
EF+ch3o2=EFs+ch3o2h	2.00E+12	0.0	17000.0
EFs=ch3cho+hco	4.17E+15	-0.9	14040.0
EF+h=EFF+h2	6.50E+05	2.4	4471.0
EF+o=EFF+oh	5.51E+05	2.5	2830.0
EF+oh=EFF+h2o	2.33E+07	1.6	-35.0
EF+ch3=EFF+ch4	1.51E+00	3.5	5481.0
EF+ho2=EFF+h2o2	9.64E+03	2.6	13910.0
EF+o2=EFF+ho2	2.00E+13	0.0	49700.0
EF+ch3o=EFF+ch3oh	5.48E+11	0.0	5000.0
EF+ch3o2=EFF+ch3o2h	4.82E+03	2.6	13910.0
c2h5+co2=EFF	4.76E+07	1.5	37410.0
c2h5o+co=EFF	1.55E+06	2.0	5734.0
EFp+h=EF	1.00E+13	0.0	0.0
EFs+h=EF	1.00E+13	0.0	0.0
EFF+h=EF	1.00E+13	0.0	0.0
ocho+c2h5=EF	1.00E+12	0.0	0.0
hco+c2h5o=EF	1.00E+12	0.0	0.0
EF=hocho+c2h4	1.00E+13	0.0	50000.0
MA+h=MA1+h2	1.50E+05	2.4	2583.0
MA+o=MA1+oh	9.50E+04	2.4	1140.0
MA+oh=MA1+h2o	1.40E+10	0.5	63.0
MA+ch3=MA1+ch4	1.50E-10	6.4	893.0
MA+ho2=MA1+h2o2	9.00E+02	2.5	10532.0
MA+o2=MA1+ho2	2.50E+12	0.0	48200.0
MA+ch3o=MA1+ch3oh	2.30E+10	0.0	2873.0

MA+ch3o2=MA1+ch3o2h	3.61E+03	2.5	10532.0
ch2co+ch3o=MA1	5.00E+11	0.0	-1000.0
MA+h=MA2+h2	9.40E+04	2.8	6280.0
MA+o=MA2+oh	9.80E+05	2.4	4750.0
MA+oh=MA2+h2o	5.25E+09	1.0	1590.0
MA+ch3=MA2+ch4	4.52E-01	3.6	7154.0
MA+ho2=MA2+h2o2	4.04E+04	2.5	16690.0
MA+o2=MA2+ho2	3.00E+13	0.0	52000.0
MA+ch3o=MA2+ch3oh	1.58E+11	0.0	7000.0
MA+ch3o2=MA2+ch3o2h	2.38E+04	2.5	16490.0
MA+c2h3=EAm+c2h4	1.00E+11	0.0	10400.0
MA+c2h5=EAm+c2h6	1.00E+11	0.0	10400.0
ch2o+ch3co=MA2	5.00E+11	0.0	-1000.0
ch3+ch3oco=MA	1.81E+13	0.0	0.0
ch3co+ch3o=MA	3.00E+13	0.0	0.0
ch3co2+ch3=MA	3.00E+13	0.0	0.0
MA1+h=MA	1.00E+13	0.0	0.0
MA2+h=MA	1.00E+13	0.0	0.0
EA+h=EAp+h2	1.88E+05	2.8	6280.0
EA+oh=EAp+h2o	1.05E+10	1.0	1586.0
EA+o=EAp+oh	1.03E+14	0.0	7850.0
EA+o2=EAp+ho2	2.00E+13	0.0	47500.0
EA+ho2=EAp+h2o2	1.68E+13	0.0	20430.0
EA+ch3=EAp+ch4	1.29E+12	0.0	11600.0
EA+c2h3=EAp+c2h4	1.00E+11	0.0	10400.0
EA+c2h5=EAp+c2h6	1.00E+11	0.0	10400.0
EA+ch3o=EAp+ch3oh	3.00E+11	0.0	7000.0
EA+ch3o2=EAp+ch3o2h	1.70E+13	0.0	20460.0
EAp=c2h4+ch3co2	1.34E+13	-0.4	24610.0
EA+h=EAs+h2	3.25E+05	2.4	4471.0
EA+oh=EAs+h2o	1.16E+07	1.6	-35.0
EA+o=EAs+oh	2.81E+13	0.0	5200.0
EA+o2=EAs+ho2	4.00E+13	0.0	47500.0
EA+ho2=EAs+h2o2	5.60E+12	0.0	17700.0
EA+ch3=EAs+ch4	3.98E+11	0.0	9500.0
EA+c2h3=EAs+c2h4	1.00E+11	0.0	10400.0
EA+c2h5=EAs+c2h6	1.00E+11	0.0	10400.0
EA+ch3o=EAs+ch3oh	3.00E+11	0.0	7000.0
EA+ch3o2=EAs+ch3o2h	2.00E+12	0.0	17000.0
EAs=ch3cho+ch3co	4.17E+15	-0.9	14040.0
EA+h=EAm+h2	1.50E+05	2.4	2583.0
EA+oh=EAm+h2o	1.40E+10	0.5	63.0
EA+o=EAm+oh	9.50E+04	2.4	1140.0
EA+o2=EAm+ho2	2.50E+12	0.0	48200.0
EA+ho2=EAm+h2o2	9.00E+02	2.5	10532.0
EA+ch3=EAm+ch4	1.50E-10	6.4	893.0
EA+c2h3=EAm+c2h4	1.00E+11	0.0	10400.0
EA+c2h5=EAm+c2h6	1.00E+11	0.0	10400.0
EA+ch3o=EAm+ch3oh	2.30E+10	0.0	2873.0
EA+ch3o2=EAm+ch3o2h	3.61E+03	2.5	10532.0
ch2co+c2h5o=EAm	5.00E+11	0.0	-1000.0
EAp+h=EA	1.00E+13	0.0	0.0
EAs+h=EA	1.00E+13	0.0	0.0
EAm+h=EA	1.00E+13	0.0	0.0
c2h5o+ch3co=EA	3.00E+13	0.0	0.0
c2h5+ch3co2=EA	3.00E+13	0.0	0.0

c2h5oco+ch3=EA	3.00E+13	0.0	0.0
EA=ch3cooh+c2h4	2.00E+13	0.0	50000.0
MF=ch2ocho+h	8.24E+19	-1.1	102500.0
MF=ch3oco+h	1.32E+19	-1.0	100100.0
MF=ch3oh+co	1.00E+14	0.0	62500.0
MF=ch3o+hco	5.37E+16	0.0	97090.0
MF=ch3+ocho	3.21E+17	-0.5	79970.0
MF+o2=ch3oco+ho2	2.00E+13	0.0	49700.0
MF+o2=ch2ocho+ho2	3.00E+13	0.0	52000.0
MF+oh=ch3oco+h2o	2.33E+07	1.6	-35.0
MF+oh=ch2ocho+h2o	5.25E+09	1.0	1590.0
MF+ho2=ch3oco+h2o2	9.64E+03	2.6	13910.0
MF+ho2=ch2ocho+h2o2	4.04E+04	2.5	16690.0
MF+o=ch3oco+oh	5.51E+05	2.5	2830.0
MF+o=ch2ocho+oh	9.80E+05	2.4	4750.0
MF+h=ch3oco+h2	6.50E+05	2.4	4471.0
MF+h=ch2ocho+h2	9.40E+04	2.8	6280.0
MF+ch3=ch3oco+ch4	1.51E+00	3.5	5481.0
MF+ch3=ch2ocho+ch4	4.52E-01	3.6	7154.0
MF+ch3o=ch3oco+ch3oh	5.48E+11	0.0	5000.0
MF+ch3o=ch2ocho+ch3oh	1.58E+11	0.0	7000.0
MF+ch3o2=ch3oco+ch3o2h	4.82E+03	2.6	13910.0
MF+ch3o2=ch2ocho+ch3o2h	2.38E+04	2.5	16490.0
MF+hco=ch3oco+ch2o	5.40E+06	1.9	17010.0
MF+hco=ch2ocho+ch2o	1.02E+05	2.5	18430.0
ch2ocho=ch3oco	2.62E+11	0.0	38180.0
ch3oco=ch3+co2	7.98E+12	0.3	15640.0
ch3oco=ch3o+co	3.18E+13	0.5	23400.0
ch2ocho=ch2o+hco	4.66E+12	0.1	27440.0